

The Simple Hückel Method and its Applications: Lecture 4

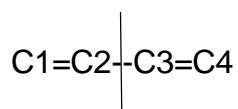
Learning outcomes:

1. Understanding longer acyclic conjugated systems
2. Use of symmetry to simplify the secular determinant.
3. Predict the allowed transitions and their polarizations.

6. 1 Longer Acyclic Conjugated Systems: Use of Symmetry

For the longer conjugated systems, the calculation of energies and coefficients is a tedious process. For butadiene, the fourth degree polynomial reduced to a quadratic equation by a simple transformation, and so the solution is not too difficult. The next even conjugated system is hexatriene and, for this, we need to solve a 6×6 determinant. Fortunately, we can take the aid of symmetry. Both *cis* and *trans* butadiene belong to different point groups, the former to C_{2v} and the latter to C_{2h} . However, since HMO theory only looks at the topology, i.e. the connectivity of the atoms, both have identical HMO energies and, consequently, wave functions. Both have C_2 axes, but whereas that of the *cis* isomer is in the molecular plane, that of the *trans* isomer is perpendicular to the molecular plane.

Since both the *cis* and *trans* isomers possess the same HMO energies and orbitals, we shall take a simplified linear model of the molecule and also ignore the hydrogens, since they do not form part of the π -conjugated system.



The vertical line represents the reflection plane (σ) that bisects the carbon atom chain. The p orbitals are labelled χ_1 , χ_2 , χ_3 and χ_4 according to the numbering of the carbon atoms. The HMO π electron Hamiltonian is invariant to reflection. In other words, σ reflection commutes with the Hamiltonian, i.e.

$$[\hat{H}, \hat{\sigma}] = 0$$

Hence, we can have simultaneous eigenfunctions of both operators. In effect, we have reduced the symmetry of the molecule from C_{2v} or C_{2h} to C_s in order to simplify the calculations. Its character table is shown below:

C_s	E	σ_h
A'	1	1
A''	1	-1

Under this reflection, χ_1 and χ_4 exchange positions, and so do χ_2 and χ_3 . Hence,

C_s	E	σ_h
χ_1	χ_1	χ_4
χ_2	χ_2	χ_3
χ_3	χ_3	χ_2
χ_4	χ_4	χ_1
$\chi(R)$	4	0

Therefore,

$$n(A') = \frac{1}{2}(4 \times 1 + 0 \times 1) = 2$$

$$n(A'') = \frac{1}{2}(4 \times 1 + 0 \times -1) = 2$$

Using the projection operator method, the two normalized symmetry adapted linear combinations (SALCs) having A' symmetry are

$$S_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_4)$$

$$S_2 = \frac{1}{\sqrt{2}}(\chi_2 + \chi_3)$$

and those with A'' symmetry are

$$S_3 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_4)$$

$$S_4 = \frac{1}{\sqrt{2}}(\chi_2 - \chi_3)$$

The first two combinations are symmetric with respect to σ reflection and the bottom two are antisymmetric. Using these SALCs, we may now construct the HMO secular determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & 0 & 0 \\ H_{21} - ES_{21} & H_{22} - ES_{22} & 0 & 0 \\ 0 & 0 & H_{33} - ES_{33} & H_{34} - ES_{34} \\ 0 & 0 & H_{43} - ES_{43} & H_{44} - ES_{44} \end{vmatrix}$$

where the H_{ij} matrix elements refer to $\langle S_i | H_\pi | S_j \rangle$ and S_{ij} to $\langle S_i | S_j \rangle$. All matrix elements with S_i 's belonging to different symmetry vanish; hence, the secular determinant is reduced to a block diagonal form. Since the SALCs are normalized and orthogonal to each other, we have

$$S_{ij} = \delta_{ij}.$$

We now evaluate the H_{ij} matrix elements.

$$\begin{aligned} H_{11} &= \langle S_1 | H_\pi | S_1 \rangle = \frac{1}{2} \langle (\chi_1 + \chi_4) | H_\pi | (\chi_1 + \chi_4) \rangle \\ &= \frac{1}{2} (\langle \chi_1 | H_\pi | \chi_1 \rangle + \langle \chi_1 | H_\pi | \chi_4 \rangle + \langle \chi_4 | H_\pi | \chi_1 \rangle + \langle \chi_4 | H_\pi | \chi_4 \rangle) = \frac{1}{2} (\alpha + 0 + 0 + \alpha) = \alpha \end{aligned}$$

$$\begin{aligned} H_{12} = H_{21} &= \langle S_1 | H_\pi | S_2 \rangle = \frac{1}{2} \langle (\chi_1 + \chi_4) | H_\pi | (\chi_2 + \chi_3) \rangle \\ &= \frac{1}{2} (\langle \chi_1 | H_\pi | \chi_2 \rangle + \langle \chi_1 | H_\pi | \chi_3 \rangle + \langle \chi_4 | H_\pi | \chi_2 \rangle + \langle \chi_4 | H_\pi | \chi_3 \rangle) = \frac{1}{2} (\beta + 0 + 0 + \beta) = \beta \end{aligned}$$

$$\begin{aligned} H_{22} &= \langle S_2 | H_\pi | S_2 \rangle = \frac{1}{2} \langle (\chi_2 + \chi_3) | H_\pi | (\chi_2 + \chi_3) \rangle \\ &= \frac{1}{2} (\langle \chi_2 | H_\pi | \chi_2 \rangle + \langle \chi_2 | H_\pi | \chi_3 \rangle + \langle \chi_3 | H_\pi | \chi_2 \rangle + \langle \chi_3 | H_\pi | \chi_3 \rangle) = \frac{1}{2} (\alpha + \beta + \beta + \alpha) = \alpha + \beta \end{aligned}$$

Similarly, it can be shown that $H_{33} = \alpha$, $H_{34} = H_{43} = \beta$ and $H_{44} = \alpha - \beta$.

These two blocks can be solved independently. The top block is

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} \equiv \begin{vmatrix} x & 1 \\ 1 & x + 1 \end{vmatrix} = 0$$

$$x^2 + x - 1 = 0 \Rightarrow x = 0.618, -1.618$$

Similarly, the other block gives the other two solutions, $x = -0.618, 1.618$. You can then determine the normalized wave functions. For example, taking the upper block and putting $x = -1.618$, we obtain

$$\begin{vmatrix} -1.618 & 1 \\ 1 & -0.618 \end{vmatrix} \begin{vmatrix} c_{11} \\ c_{12} \end{vmatrix} = 0$$

$$\Rightarrow -1.618c_{11} + c_{12} = 0 \Rightarrow c_{12} = 1.618c_{11}$$

Using the normalization condition

$$c_{11}^2 + c_{12}^2 = 1 \Rightarrow c_{11}^2 + 1.618^2 c_{11}^2 = 1 \Rightarrow c_{11} = \frac{1}{\sqrt{1 + 1.618^2}} = 0.5257$$

$$c_{12} = 1.618c_{11} = 0.8506$$

Therefore,

$$\begin{aligned} \phi_1 &= 0.5257s_1 + 0.8506s_2 = 0.5257 \left(\frac{1}{\sqrt{2}} (\chi_1 + \chi_4) \right) + 0.8506 \left(\frac{1}{\sqrt{2}} (\chi_2 + \chi_3) \right) \\ &= 0.3717(\chi_1 + \chi_4) + 0.6015(\chi_2 + \chi_3) \\ &= 0.3717\chi_1 + 0.6015\chi_2 + 0.6015\chi_3 + 0.3717\chi_4 \end{aligned}$$

The other wave functions can be similarly obtained.

For butadiene, we could have used the full point group (C_{2h} for the *trans* isomer and C_{2v} for the *cis* isomer) to obtain the same SALCs since the molecules belong to simple point groups. For more complex molecules, using a simpler sub-group may be helpful.

While symmetry factoring may not appear to be advantageous for butadiene, it greatly simplifies calculations for the higher polyenes. For example, the secular determinant for hexatriene is reduced to two 3×3 blocks, one containing the symmetric linear combination and the other to the antisymmetric one.

6.2 Even Number of Carbon Atoms

After butadiene, the next higher conjugated system having an even number of carbon atoms would be the conjugated triene, i.e. 1,3,5-hexatriene.

trans-1,3,5-hexatriene

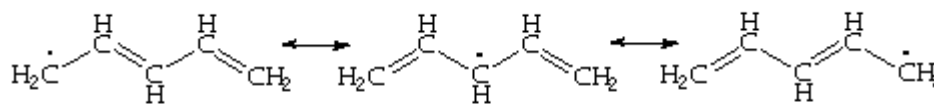


You should anticipate by now that with six carbon atoms there would be six π MOs, three of which would be bonding and three anti-bonding. The anti-bonding MOs would each be paired with a bonding molecular orbital (BMO), in terms of symmetry about the nonbonding level. The number of nodes would increase in the sequence 0, 1, 2, 3, 4, 5 in order of the increasing energies of the MOs. Since the lowest energy molecular orbital (LUMO) of butadiene was considerably lower in energy than that of ethene, you could also expect that a continued increase in the length of the conjugated system would continue to drop the energy of the triene LUMO and correspondingly increase the energy of its paired highest occupied molecular orbital (HOMO) (Fig. 3).

Exercise 4 Draw out the energy level diagram for a triene system and compare it with the corresponding diene system. Also, write the point group of the hexatriene molecule, assuming that it is in the all-trans configuration shown above.

6.3. Odd Number of Carbon Atoms.

Just as the allyl system had an odd number of carbon atoms (three) in the conjugated system, there are also conjugated systems having 5, 7, etc. carbon atoms. The pentadienyl system is the simplest of these.



Resonance structures for the pentadienyl radical

The main difference between these odd carbon systems and the even carbon ones is that the odd carbon systems (which can have, like the allyl system, a carbocation, a

radical, and an anion) have a nonbonding Molecular Orbital (NBMO). Like the allyl radical, the pentadienyl radical has its odd electron in the NBMO, so we only need to know the coefficients of the NBMO in order to predict the odd electron density in this radical, or for that matter the positive charge density in the carbocation and the negative charge density in the carbanion. Incidentally, this latter circumstance may be somewhat non-intuitive. The radical, which has 1 electron in the NBMO is, as a hydrocarbon radical would be expected to be, nonpolar, i.e. it has zero charge on every atom since, as we have seen for all the systems studied so far, $q_r = 1$ in the neutral species for all atoms. Consequently, $Q_r = 0$ for every atom. So, if one adds one electron to form the anion, it is added to the NBMO and the result is that the negative charge is determined by the distribution of this electron in the NBMO. Similarly, if one electron is removed from the radical to generate the carbocation, it is removed from the NBMO, so the positive charge is generated at the positions determined by the electron density in the NBMO.

Exercise 5. Find the coefficients of the pentadienyl system. Use these to calculate the spin distribution in the pentadienyl radical and the charge distributions in the cation and anion. Compare these with the results predicted from resonance theory (i.e., write the three resonance structures for the radical, carbocation and anion).

6.4 The resonance integral β

The HMO method is an empirical method. It computes the molecular orbital energies in terms of two parameters: α and β . The coulomb integral α represents the energy of an electron in a “free” carbon 2p AO in a molecule. Its value is ~ -11.4 eV. The resonance integral β is a composite parameter representing the electron-nucleus attraction, the interelectronic repulsion and the kinetic energy. Its value for adjacent 2p orbitals $H_{ij}(\text{C}=\text{C}) \sim -3$ eV.

In HMO theory, the electronic transition energies are computed in terms of the empirical parameter β . The value of β can be determined by comparing the spectral energies for a series of homologous compounds and then finding the value of β that best fits the data. Different values of β have been determined depending on the data used for the calculation.

6.7 Generalizations

The energy levels and molecular orbitals for polyenes having 2-6 carbon atoms are depicted in Figure 3.

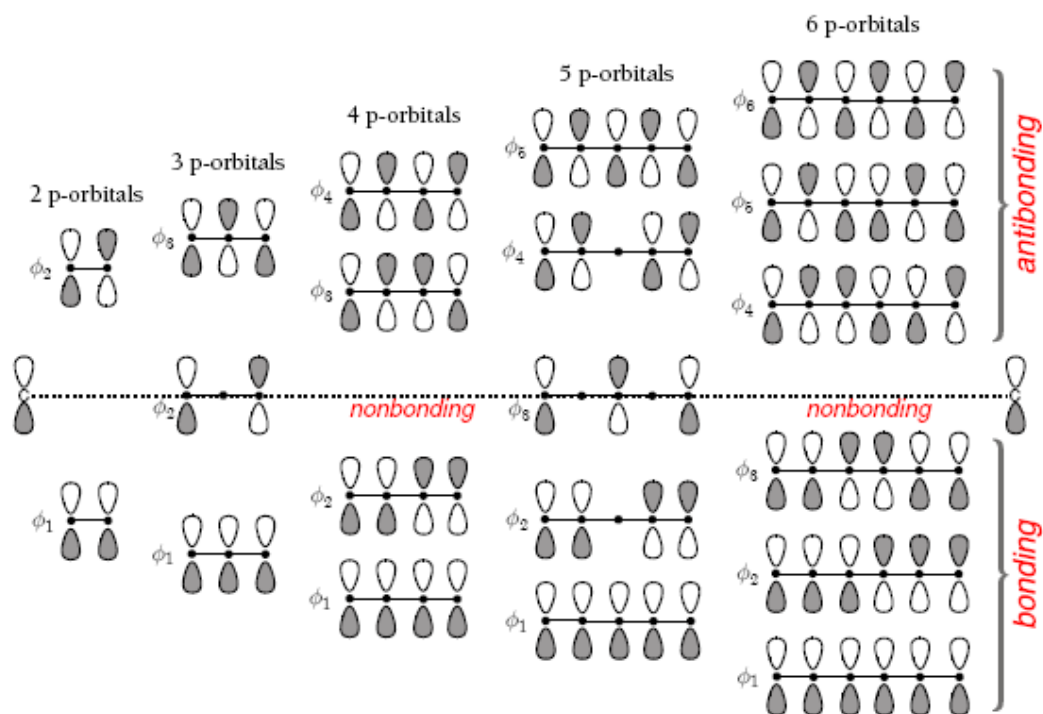


Figure 3. HMO schemes for conjugated chains involving 2 – 6 carbon atoms.

While discussing the pericyclic reactions of these polyenes, it is useful to know a little bit about their HMOs.

Some generalizations are given below:

- (1) There are no nodes in the lowest energy MO. With each higher MO, one additional node is added. The more the number of nodes, the higher is the orbital energy. This is a fundamental concept in chemistry.
- (2) The anti-bonding MOs are paired with a bonding molecular orbital (BMO), in terms of symmetry about the nonbonding level. In the case of odd carbon atom systems, there is a nonbonding MO.

(3) As a consequence of (2), the sum of all roots is zero. Another generalization is that none of the roots can exceed 4, i.e. $|x_j| \leq 3$ or $(\alpha - 3\beta) \leq \varepsilon_j \leq (\alpha + 3\beta)$.

(4) The number of nodes increases in the sequence 0, 1, 2, 3, 4, 5 in order of the increasing energies of the MOs.

6.5 Spectroscopy

Though we had reduced butadiene to a simpler point group for the purpose of determining its energy levels, one needs to use the full point group to find the irreducible representations of the wave functions and the allowed transitions.

For spectroscopy of ethylene, *cis*- and *trans*-butadiene, you are referred to

http://epgp.inflibnet.ac.in/epgpdata/uploads/epgp_content/S000005CH/P000663/M010518/ET/1454932515CHE_P8_M33_e-Text.pdf

<https://epgp.inflibnet.ac.in/Home/ViewSubject?catid=5>

Kakkar, Rita (2015) *Atomic and Molecular Spectroscopy*. Cambridge University Press.

References

<http://research.cm.utexas.edu/nbauld/unit1.htm>

You may also consult the ePG-pathshala lectures at

http://epgp.inflibnet.ac.in/epgpdata/uploads/epgp_content/chemistry/02.physical_chemistry-i_/30.huckel_molecular_orbital_theory-introduction/et/6376_et_che_p2_m30_etext.pdf

http://epgp.inflibnet.ac.in/epgpdata/uploads/epgp_content/chemistry/02.physical_chemistry-i_/31.huckel_molecular_orbital_theory_application_part-i/et/6377_et_che_p2_m31_etext.pdf

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However, there is a problem with the notation. We are following the notation prescribed by IUPAC (International Union of Pure and Applied Chemistry) and that is correct.

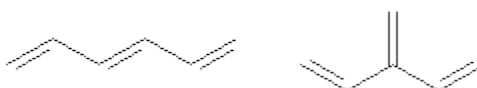
8. Exercises

1. Calculate the energy separation between the HOMO and LUMO in units of β for all the compounds in the following table:

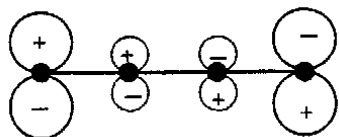
Compound	λ	HOMO	LUMO	LUMO-HOMO	$\tilde{\nu}$
Ethylene	161 nm				
Buta-1,3-diene	217 nm				
Hexa-1,3,5-triene	244 nm				
Octa-1,3,5,7-tetraene	303 nm				

Obtain the best slope of the function β versus $\tilde{\nu}$ and hence determine β .

2. Compare the total π energies and π bond orders in 1,3,5-hexatriene and 3-methylene-1,4-pentadiene. What can you conclude about the effects of branching in a conjugated π system?

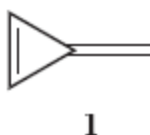


3. Which orbital of butadiene is represented below?



Explain.

4. Methylene cyclopropene, **1**, is a hydrocarbon that, despite its simplicity, was isolated only in the last decades.



Examine whether the following secular determinant of **1** is correct or incorrect

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 1 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix}$$

5. (a) Calculate the total π -electron energy of ethylene in the

- (i) ground state
- (ii) singly excited state

(b) Calculate the total π -electron energy of the dianion $\text{C}_2\text{H}_4^{2-}$.

(c) The electronic transition from the ground to excited state in ethylene occurs at 165 nm. Calculate a value for β (in kJ/mol) based on the absorption of ethylene.

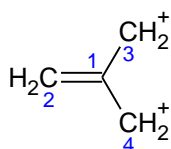
(d) Use simple Group Theoretical arguments to decide whether the the ($\pi \rightarrow \pi^*$) transition in ethylene is allowed:

6. (a) Identify the ground and excited states of the same spin multiplicity for the *cis*-butadiene molecule.

(b) Which spin-allowed transitions are electric-dipole allowed and with what polarization?

7. Write down the Hückel secular determinant for 1,3-butadiene. Calculate the energies of the Hückel molecular orbitals of 1,3-butadiene in terms of α and β . Also, calculate the delocalization energy.

8. Consider trimethylene methane molecule



(i) Write down the Hückel secular determinant for the molecule using the numbering scheme shown.

(ii) Find the energies of the molecular orbitals.

(iii) Draw a molecular orbital diagram showing the energies of the molecular orbitals, and how the four π electrons occupy these orbitals. Comment on the electronic structure of the compound.

(iv) Calculate the delocalization energy of trimethylenemethane. Butadiene and trimethylenemethane are structural isomers. Which compound is expected to be more stable and why?

9. The occupied Hückel π molecular orbitals of 1,3-butadiene can be written as

$$\begin{aligned}\phi_1 &= 0.3717\chi_1 + 0.6015\chi_2 + 0.6015\chi_3 + 0.3717\chi_4 \\ \phi_2 &= 0.6015\chi_1 + 0.3717\chi_2 - 0.3717\chi_3 - 0.6015\chi_4\end{aligned}$$

Using the Hückel approximation, show that ϕ_1 is normalized. Sketch both ϕ_1 and ϕ_2 . State, with reason, which orbital is lower in energy. Calculate the Hückel π bond order between the central carbon atoms (atoms 2 and 3) and between two other adjacent atoms (e.g. atoms 1 and 2). Comment on the values obtained in relation to a simple drawing of the structure of 1,3-butadiene.